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Determination of Residual Alkalinity in Positive and Negative Electrodes of a Worked-out Nickel–Iron Battery

A. I. Demidov, M. S. Kokhatskaya, and Sun Lyu Bin

St. Petersburg State Polytechnic University, St.Petersburg, Russia

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Abstract—The content of sodium carbonate and sodium hydrocarbonate in the active paste of the positive and negative electrodes of a worked-out nickel–iron battery after their prolonged storage in air was determined by means of a conductometric analysis.

Nickel–iron battery suggested by Edison at the beginning of the last century belongs to alkaline lamellar cells, in which potassium and sodium hydroxide solutions with a reasonably high electrical conductivity in a wide temperature range are commonly used as electrolytes [1]. The use of the sodium electrolyte is due to its favorable influence on the nickel oxide electrode at elevated temperatures. The potassium electrolyte is preferable at low temperatures owing to its higher electrical conductivity and lower freezing point [2]. The drawback of alkaline electrolytes is their susceptibility to carbonization, which mainly occurs via absorption of atmospheric carbon dioxide and results in accumulation of a carbonate in the electrolyte in the course of operation of a battery [1].

Prolonged storage of positive and negative electrodes of worked-out nickel–iron batteries in air leads to further carbonization of the electrolyte remaining in pores of the active paste. As a result, sodium hydroxide is converted into carbonate and then hydrocarbonate by the reaction:

$$2NaOH + CO_2 \rightarrow Na_2CO_3 + H_2O,$$
$$Na_2CO_3 + H_2O + CO_2 \rightarrow 2NaHCO_3.$$

In hydrometallurgical processing of worked-out electrodes of nickel–iron batteries, it is necessary to know the residual content of carbonate and bicarbonate in the active paste, because their amount affects the expenditure of sulfuric acid for recovery of positive electrodes containing nickel hydroxide and the quality of the active paste of the negative electrode, obtained in processing.

In this study, the content of sodium carbonate and bicarbonate in the active paste of the positive and negative electrodes of a worked-out nickel–iron battery was determined by conductometric titration.

Titration, which underlies the classical titrimetric analysis, is a virtually versatile technique widely applied in physicochemical analytical techniques. In these methods, the electrical parameters of the systems being analyzed, which change as a result of chemical reactions, are measured and recorded [3]. To these techniques belongs conductometric titration, in which the equivalence point is found by measuring the change in the electrical conductivity of a solution during the reaction of the titrant with the substance to be determined. The equivalence point is determined from the sharp break in a titration curve, which reflects the change in the electrical conductivity of the solution being analyzed upon addition of a titrant in the course of titration [4].

We used in the study the active paste extracted from lamellas of a worked-out nickel–iron battery of the TNZh-250-U2 type and chemically pure sulfuric acid. The content of carbonate and hydrocarbonate in the active paste of the worked-out electrodes kept in contact with air for a long time was determined by conductometric titration of the filtrate obtained upon treatment of the active paste with distilled water. In the course of the experiment, the solution was vigorously agitated with a magnetic stirrer and its resistance was measured using an E7-15 immittance meter with the use of graphite electrodes. No less than 5–7 experiments were carried out in parallel.

During the titration of a filtrate containing sodium carbonate and hydrocarbonate with a standard solution of sulfuric acid, first, sodium carbonate reacts with the strong acid to yield sodium hydrocarbonate and sulfate. Then, sodium bicarbonate contained in the ini-

tial solution and sodium carbonate obtained in titration are neutralized to give sodium sulfate.

To construct the theoretical dependence of the electrical resistivity of the solution on the number of titrant equivalents, we suggested in this study that the electrical conductivity of the initial solution is a sum of the electrical conductivities of the corresponding salts, i.e., $\chi_\Sigma = \chi_{Na_2CO_3} + \chi_{NaHCO_3}$, where χ_Σ is the total electrical conductivity of the initial solution, and $\chi_{Na_2CO_3}$ and χ_{NaHCO_3} are the electrical conductivities of sodium carbonate and sodium hydrocarbonate solutions, respectively. The calculation was performed for solutions containing equivalent amounts of sodium carbonate and hydrocarbonate (0.01, 0.02, 0.05, and 0.1 N) [5].

During titration, the electrical conductivity of the solution varies as follows: Before the first equivalence point, at $0 < y < 1$,

$$\chi_\Sigma = \chi_{Na_2CO_3}(1 - y) + \chi_{NaHCO_3}(1 + y) + \chi_{Na_2SO_4}y,$$

where $\chi_{Na_2SO_4}$ is the electrical conductivity of the sodium sulfate solution, and y, the number of titrant equivalents.

At the first equivalence point, at $y = 1$,

$$\chi_\Sigma = 2\chi_{NaHCO_3} + \chi_{Na_2SO_4}.$$

In titration to the second equivalence point, at $1 < y < 3$,

$$\chi_\Sigma = \chi_{NaHCO_3}(3 - y) + \chi_{Na_2SO_4}y.$$

At the second equivalence point, at $y = 3$,

$$\chi_\Sigma = 3\chi_{Na_2SO_4}.$$

In titration after the second equivalence point, at $3 < y < 5$,

$$\chi_\Sigma = 3\chi_{Na_2SO_4} + \chi_{H_2SO_4}(y - 3),$$

where $\chi_{H_2SO_4}$ is the electrical conductivity of sulfuric acid.

The resulting values of the total electrical conductivity were used to construct the theoretical dependences of the electrical conductivity of the solutions on the number of titrant equivalents (Fig. 1). As can be seen, the titration curves for dilute solutions of sodium carbonate and sodium hydrocarbonate (0.01 and 0.02 N) show two clearly pronounced inflections at the first and the second equivalence points, respectively.

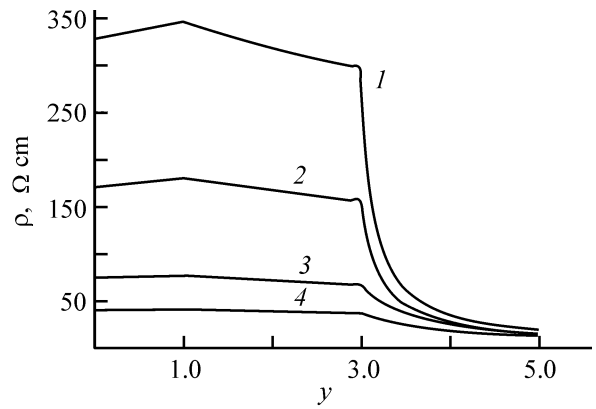

Fig. 1. Theoretical dependence of the electrical resistivity ρ of the solution on the number of titrant equivalents, *y*, taken during titration of a solution containing sodium carbonate and sodium hydrocarbonate at a ratio of 1 : 1 with 0.1 NH_2SO_4 at 25°C. Concentration (g-equiv l^{-1}): (*1*) 0.01, (*2*) 0.02, (*3*) 0.05, and (*4*) 0.1.

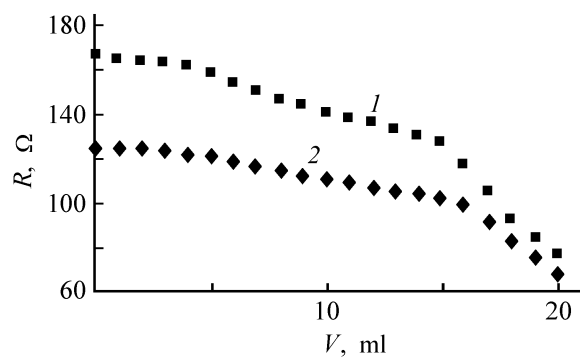

Fig. 2. Conductometric titration curves of the filtrate obtained by treating the active paste of the positive electrode with distilled water. (*R*) Resistance; (*V*) titrant volume. Experiments: (*1*) initial and (*2*) after half a year.

In the experiments, a 2-g portion of the active paste was placed in distilled water, the solution was filtered, and the titration was performed with a standard solution of 0.1 N sulfuric acid. In each titration, the readings of the immitance meter were recorded and the values obtained were used to plot the titration curves and to calculate the residual alkalinity of the solution. The dependences obtained in conductometric titration are shown in Fig. 2. As can be seen, the curves have two inflections at the two equivalence points.

Comparison of the calculated titration curves with the experimental curves shows their identical character. As can be seen from Fig. 2, the amount of carbonate in the solution decreases in the course of time, whereas the amount of bicarbonate increases.

The amount of sulfuric acid spent for titration was calculated from the curves of conductometric titration,

and the amount of sodium carbonate and bicarbonate in a weighed portion of the active paste was calculated from the equivalence law. The content of sodium carbonate and hydrocarbonate was $(6.1 \pm 1.0)\%$ and $(7.3 \pm 1.0)\%$ in the positive electrode and (0.8 ± 0.2) and $(2.2 \pm 0.2)\%$, respectively, in the negative electrode.

It was established for the example of the active paste of the positive electrode that sodium carbonate is converted into bicarbonate in electrodes of worked-out nickel–iron batteries stored in air for a long time. As a result, the content of sodium carbonate in the active paste decreases, and that of sodium hydrocarbonate, increases. A repeated analysis of the active paste of a worked-out positive electrode, made in half a year, demonstrated that the content of sodium carbonate and hydrocarbonate in the active paste changed to $(5.7 \pm 0.6)\%$ and $(9.0 \pm 0.6)\%$, respectively.

CONCLUSIONS

(1) The content of sodium carbonate and sodium hydrocarbonate in the active paste of positive and negative electrodes of a worked-out nickel–iron battery was determined by conductometric titration.

(2) It was established for the example of the active paste of a positive electrode that the content of sodium carbonate in the active paste in electrodes of worked-out nickel–iron batteries stored in air for a long time decreases, and that of sodium bicarbonate increases.

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